Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1994, **4(5)**, 185–186
Mendeleev Communications

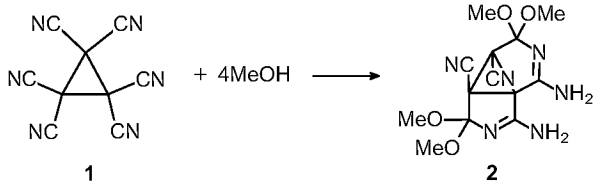
Two Alternative Pathways for the Interaction of Hexacyanocyclopropane with Nucleophiles

Oleg E. Nasakin,*[a] Petr M. Lukin,[a] Evgenii V. Vershinin,[a] Sergei V. Lindeman[b] and Yurii T. Struchkov[b]

[a] *Chuvash State University, 428015 Cheboksary, Russian Federation.*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation. Fax: +7 095 135 5085*

Methanol molecules add to the cyano groups of hexacyanocyclopropane **1** in the presence of sodium methylate to give 1,4-adduct **2**. The interaction of **1** with *N*-methylpyridinium iodide leads to opening of the cyclopropane ring and to the formation of propenide **3** and iodine cyanide **4**; the structure of **2** was established by an X-ray crystallographic study.

Previously we have reported the synthesis of hexacyanocyclopropane **1** and solved its crystal structure.[1] An X-ray investigation of a single crystal of compound **1** grown from 1,4-dioxane showed it to represent a 1:3 solvate with the oxygen atoms of dioxane coordinated to two carbon atoms in the cyclopropane ring of **1** and to two geminal carbon atoms of the cyano groups. Thus, it could be supposed that both carbon atoms of the cyano groups and the carbon atoms of the cyclopropane ring of **1** can take part in chemical reactions.



1 **2**

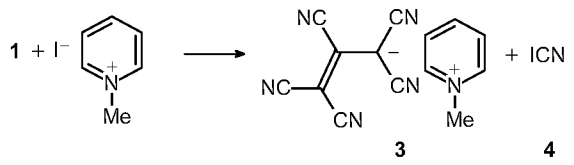
Indeed, we have carried out reactions of **1** with nucleophiles by these two alternative pathways.

Methanol reacts with the cyano groups of **1** in the presence of sodium methylate to give the 1:4-adduct, 2,9-diamino-4,4,7,7-tetramethoxy-5,6-dicyano-3,8-diazatricyclo[4,3,0,$0^{1,5}$]-nona-2,8-diene **2**.† The structure of **2** (Fig. 1) has been

† *Preparation of compound* **2**. Compound **1** (0.005 mol) was added dropwise to a stirred solution of sodium (0.002 g) in methanol (5 ml) at a temperature not exceeding 40 °C. On dissolution of compound **1** the reaction mixture was cooled to 0–5 °C. The precipitate obtained was filtered off and washed with cold methanol. A crystalline product was recrystallised from methanol and dried *in vacuo* to give compound **2** (0.62 g) in 39% yield with m.p. 127–128 °C (decomp.). IR spectral data (vaseline oil, cm^{-1}): 3455, 3410, 3360, 3165 (ν_{NH_2}), 2265 ($\nu_{C\equiv N}$), 1660, 1645, 1610 ($\nu_{C=N}$, δ_{NH_2}), 1190, 1125, 1090, 1055 (Me–O–C–O–Me). Single crystals for X-ray investigation were grown from methanol and had a satisfactory elemental analysis.

determined by an X-ray study of the monocrystal.[‡]

Interaction of compound **1** with *N*-methylpyridinium iodide leads to opening of the cyclopropane ring and to the formation of *N*-methylpyridinium pentacyanopropenide **3** and iodine cyanide **4**. Compound **3**[§] is identical with *N*-methylpyridinium pentacyanopropenide obtained from tetracyanoethylene.[4]



3 **4**

Financial support by the Russian Foundation for Fundamental Researches (grant no. 93-03-4006) is gratefully acknowledged.

[‡] *Crystal data for* **2**: $C_{13}H_{16}N_6O_4$, MeOH, orthorhombic, space group *Pbca*, at 153 K, $a = 11.942(6)$, $b = 13.887(8)$, $c = 21.23(1)$ A, $D_c = 1.329$ g cm^{-3}, $Z = 8$, $F(000) = 1488$. 3117 independent reflections were measured with a Siemens P3/PC automated diffractometer (153 K, λMoKα, graphite monochromator, θ/2θ-scan, $2\theta \leqslant 50°$). The structure was determined by a direct method and refined by a full-matrix least-squares technique with an anisotropic approximation for non-hydrogen atoms. All hydrogen atoms and solvating methanol molecules were located in the difference Fourier synthesis. Hydrogen atoms were refined isotropically with common $U_{iso} = 0.03$ A^2 (for methyl hydrogens 0.05 A^2). The refinement converged at $R = 0.040$, $R_w = 0.042$ for 2320 reflections with $F^2 \geqslant 2\sigma$. All calculations were carried out using the SHELXTL PLUS program package[2] on an IBM PC computer. Atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (see Notice to Authors, *Mendeleev Commun.*, 1994, issue 1).

[§] *Interaction of* **1** *with* N-*methylpyridinium iodide*. Compound **1** (0.005 mol) was dissolved in ethyl acetate (3 ml). *N*-Methylpyridinium iodide was added dropwise to the stirred solution and the reaction mixture was heated up to 40 °C. On dissolution of *N*-methylpyridinium iodide the reaction mixture was cooled to 0 °C and the precipitate obtained was filtered off. The crystalline product was then purified by recrystallization from water–ethanol (3:1) to give compound **3** (0.9 g) in 69% yield, m.p. 160–161 °C (in agreement with ref. 3). Compound **3** is identical in its IR spectroscopic and TLC (R_f 0.63; EtOAc–EtOH, 1:1) data with *N*-methylpyridinium pentacyanopropenide obtained by the procedure described in ref. 3. IR (vaseline oil; ν/cm^{-1}): 2255, 2210 (C≡N); 1620 and 1570 (C=C and C=N). In order to prove the formation of **4**, ethyl acetate was evaporated from the filtrate to yield a solid which was purified by vacuum sublimation to give compound **4** (0.2 g) with m.p. 148–149 °C (lit.,[4] 147–149 °C).

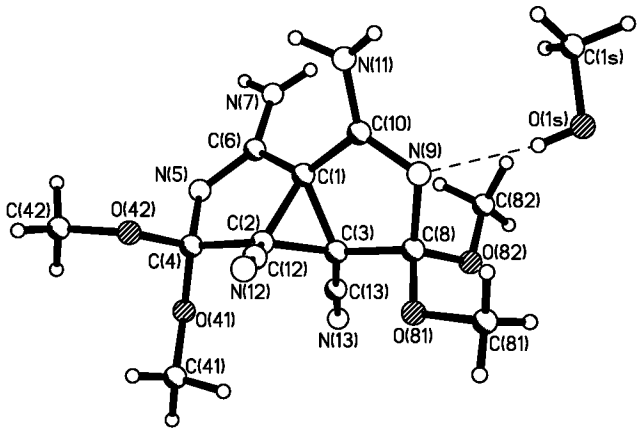


Fig.1 Molecular structure of **2** (hydrogen bonds shown by a dashed line). Selected bond lengths/A: C(1)–C(2) 1.512(3), C(1)–C(3) 1.509(3), C(1)–C(6) 1.487(3), C(1)–C(10) 1.496(3), C(2)–C(3) 1.517(3), C(2)–C(4) 1.561(3), C(3)–C(8) 1.558(3), C(4)–N(5) 1.443(3), C(6)=N(5) 1.297(3), C(6)–N(7) 1.325(3), C(8)–N(9) 1.451(3), C(10)=N(9) 1.289(3), C(10)–N(11) 1.323(3). Hydrogen bond parameters: N(9)···O(1S) 2.859(3) A, N(9)···H(O(1S)) 2.08(3)A, N···H–O angle 167(4)°.

References

1 V. M. Anisimov, A. B. Zolotoi, M. Y. Antipin, P. M. Lukin, O. E. Nasakin and Yu. T. Struchkov, *Mendeleev Commun.*, 1992, 24.
2 W. Robinson and G. M. Sheldrick, SHELX in: *Crystallographic Computing Techniques and New Technologies*, eds. N. W. Isaacs and M. R. Taylor, Oxford, England, Oxford University Press, 1988, p. 366.
3 W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhard, *J. Am. Chem. Soc.*, 1958, **80**, 2795.
4 W. J. Linn, O. W. Webster and R. E. Benson, *J. Am. Chem. Soc.*, 1965, **87**, 3651.

Received: Moscow, 25th April 1994
Cambridge, 3rd June 1994; Com. 4/02911I